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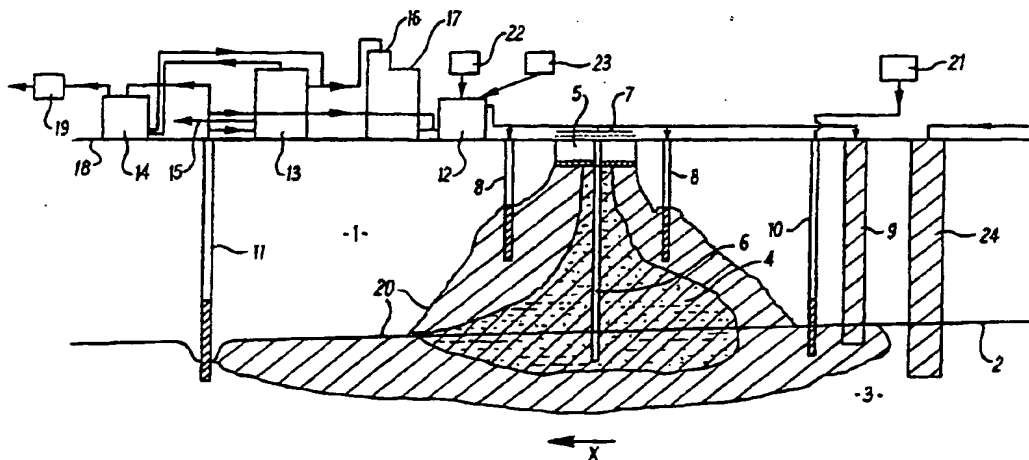
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(71) Applicant (for all designated States except US): BRITISH NUCLEAR FUELS PLC (GB/GB); Risley, Warrington, Cheshire WA3 6AS (GB).		Published With international search report.	
(72) Inventor; and (75) Inventor/Applicant (for US only): ECCLES, Harry (GB/GB); British Nuclear Fuels plc, Springfields Works, Salwick, Preston PR4 0XJ (GB).			
(74) Agent: McCORMACK, Derek, James; British Nuclear Fuels plc, Intellectual Property & Patents, Risley, Warrington, Cheshire WA3 6AS (GB).			

(54) Title: PROCESS FOR THE TREATMENT OF CONTAMINATED MATERIAL



(57) Abstract

A process for the decontamination of a medium comprising a material contaminated with one or more organic species and one or more metal species comprises the steps of treating a body of the said medium by a process which breaks down the organic contaminant(s) by or through the action of microbial agents followed by treating the same body with microbially produced sulphuric acid so as to solubilise and leach the metal species as a metal sulphate and treating the leached metal sulphate by a bioprecipitation process which converts the said sulphate to one or more insoluble metal sulphides.

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Process for the treatment of contaminated material

The present invention relates to a process for the treatment of contaminated material, in particular a process for the treatment of organic and metal, especially heavy metal, contaminants in bulk particulate material such as land or soil using biochemical processes.

World-wide, substantial amounts of land have been contaminated with both organic and inorganic substances as a result of industrial, waste disposal and other activities. Examples of such contaminants include: toxic heavy metals including mercury, cadmium, barium and lead, radionuclides such as actinides and fission products and organic pollutants such as btex (benzene, toluene, ethylbenzene and xylene), PAHs (polyaromatic hydrocarbons), polychlorinated biphenyls (PCBs) and dioxins. Such contaminants can pose a significant threat to ground water and therefore drinking water supplies and in many cases either limit, or prevent land re-use. Additionally, as a result of recent legislation in the United States of America and likely similar legislation within the European Community and elsewhere, waste producers are becoming increasingly liable to prosecution and to meet the costs of recovery and clean up if they do not act responsibly towards their wastes. Consequently there is a growing need for technologies which can solve the problem of contaminated land.

To date, a number of techniques have been developed to remediate contaminated land. Examples include: soil stabilisation, electromigration, vitrification, volatilisation, incineration, soil washing, pump and treat systems, land farming, slurry phase bioremediation etc. Many of these known techniques possess several limitations including:

- a) Lack of a permanent solution to the problem, eg transferral of the material to a toxic landfill, or entrapment within matrixes possessing a limited life;

- b) Unsuitability to treat a wide range of contaminants, eg metal contaminated land in the case of current biological processes;
- c) The generation of high volume, or difficult to control secondary wastes, eg soil stabilisation and incineration;
- d) Lack of selectivity of in-situ or ex-situ options as appropriate to a particular site, eg as in the case of incineration or soil washing;
- e) High costs, eg incineration, vitrification and pump and treat systems;
- f) Limited ability to re-use contaminants, eg soil stabilisation systems when applied to metals.

The present invention seeks to address these problems by enabling biological systems to remediate metal and organic contaminated media such as land non-specifically.

According to the present invention a process for the decontamination of a medium comprising a material contaminated with one or more organic species and one or more metal species comprises the steps of treating a body of the said medium by a process which breaks down the organic contaminant(s) by or through the action of microbial agents followed by treating the same body with microbially produced sulphuric acid so as to solubilise and leach the metal species as a metal sulphate; and treating the leached metal sulphate by a bioprecipitation process which converts the said sulphate to one or more insoluble metal sulphides. Desirably, the process also includes the following steps:

- a) the separation of hydrogen sulphide from the insoluble metal sulphides.
- b) the subsequent oxidation of the separated hydrogen sulphide to form a reusable source of sulphur containing ingredient.

In the said process organic contaminants may also be broken down by the action of microbially produced

sulphuric acid in the second (metal species removal) stage of the process.

In the first or organic degradation stage of the process the pH of the medium being treated is desirably in the range 4 to 9. The micro-organisms which break down the organic compounds may be present in the said medium as naturally occurring species, eg as bacteria present in soil, or cultures of them may be added to the said medium. In either case, nutrients are desirably fed to promote the activity of the appropriate species. The microbial consortia employed will depend upon the type of organic contaminant present, which may be determined by prior analysis of the said medium, and the nutrients will be selected accordingly. The enrichment of the medium by addition of different types of micro-organism to break down the organic contaminants present is described further below.

The organic contaminants may comprise, for example, benzene, toluene, other aromatic compounds, PAHs or any of the other common organic contaminants referred to above.

The medium to be decontaminated may comprise a particulate material such as soil, rock particles, dredgings, sediments, sludges, process residues, slags from pyrolytic processes, furnace dusts and the like. The contaminants may be contained on the surface of the particulate material or may be bound inside the particles thereof.

Several metal species may be present in the said medium and these may be converted to various metal sulphates and subsequently bioprecipitated as various metal sulphides. The term "metal species" as used herein includes metals, alloys, metal salts, metalloids and metal containing compounds and complexes.

The said metal species contaminants may include:

- i) actinides or their radioactive decay products or compounds thereof;

- ii) fission products;
- iii) heavy metals or compounds thereof.

Actinides are elements having periodic numbers in the inclusive range 89 to 104.

The term 'fission product' as used herein refers to those elements formed as direct products (or so-called 'fission fragments') in the fission of nuclear fuel and products formed from such direct products by beta decay or internal transitions. Fission products include elements in the range from selenium to cerium in the Periodic Table.

Non-radioactive heavy metals desired to be separated by the process of the present invention include toxic metals such as nickel, zinc, cadmium, copper, mercury and cobalt. These are commonly found as earth contaminants or in aquatic sediments near industrial plants which have employed chemicals containing these elements and on waste disposal sites. The metallic contaminants separated by the process of the present invention may include a mixture of radioactive and non-radioactive metallic contaminants.

The particulate material desirably is treated by leaching with the biologically produced sulphuric acid using an aqueous leachant solution.

Where the medium to be decontaminated comprises soil or land, this may be treated in-situ or ex-situ. In the latter case the soil may be pre-treated eg to remove or crush large objects eg boulders, stones and the like. A suitable mixture of an aqueous solution containing biologically produced sulphuric acid and/or a source of sulphurous material bioconvertible into sulphuric acid may be injected into or mixed with the soil. Other ingredients such as nitrogen-rich or phosphorus-rich materials and air may optionally be added. The bioconversion may be carried out in a known way by microbial agents present in the soil. The sulphurous material may comprise either elemental sulphur or another

reduced form of sulphur. Some addition of nutrients may be required to promote the microbial action necessary for organics degradation. The precise nature of these additions will be site specific and selected accordingly.

Where the soil or other particulate material, eg process residues or slag, is to be treated ex-situ it may be treated in one or more suitable known reactors. The aforementioned ingredients may be added to promote organics removal and acid production.

Where the bioconversion to produce sulphate ions is carried out in the soil to be treated it may be brought about by the action of naturally occurring sulphur oxidising organisms including: *Thiobacillus ferrooxidans*, *Thiobacillus thiooxidans* and *Thiobacillus neapolitanus*. These organisms obtain the energy necessary for their growth by the oxidation of reduced forms of sulphur thereby producing sulphates and sulphuric acid, or by the oxidation of ferrous iron to ferric iron.

If the soil is deficient in appropriate micro-organisms, or if the particulate material is to be treated in a separate bioreactor then these micro-organisms may be added as a mixed consortium obtained from similar soil environments.

In addition to acid leaching mentioned above metal release can occur by one or more of the following mechanisms:

- a) direct attack of metal sulphides;
- b) by electrochemical processes (galvanic conversion), resulting from contact between two dissimilar metal species immersed in a suitable electrolyte, eg sulphuric acid; or
- c) by the oxidative effect of ferric sulphate.

As an alternative to in-situ biological acid production, the sulphuric acid required for the leaching process may be produced chemically or biochemically in a

separate bioreactor and added to the soil or other particulate material after production.

During process start up, elemental sulphur, or sulphuric acid (bypassing in-situ biological acid production), may be used as the acid source for leaching. Thereafter, elemental sulphur or a combination of elemental sulphur and sulphuric acid may be the major acid source. Elemental sulphur, or sulphuric acid may be added to replace the available sulphur lost from the system, as metal sulphides.

The leachate solution may be allowed to percolate through and drain from the body of particulate material. The leachate solution so collected may then either be re-circulated through the particulate material or be pumped into a reactor to carry out the bioprecipitation process.

The bioprecipitation step in the process of the present invention may be a known step per se which may employ a naturally occurring consortium of dissimilatory sulphate reducing bacteria (SRB), to convert aqueous metal sulphates to metal sulphides. Micro-organisms responsible for this transformation include: species of *Desulfovibrio* and *Desulfomonas* and may be grown in an enclosed bioreactor system. These organisms oxidise simple organic compounds such as lactic acid and ethanol, to derive the energy necessary for their growth. However, more complex carbon sources can occasionally be used, eg phenolic compounds, or possibly organic materials leached from the soil during bioleaching. As a consequence of this oxidation, sulphates are reduced to sulphides and water. As the sulphides of many heavy metals possess low solubilities in aqueous solution, these precipitate together with some biomass as a sludge within the bioprecipitation reactor. The metal sulphides will normally be separated as sludge and may be recovered and sold for metal recovery, or in the case of toxic or

radioactive metals, further immobilised in a subsequent process.

Reduction of sulphuric acid entering the bioprecipitation stage, eg reactor, from the metal leaching step will result in the production of hydrogen sulphide and consequent reduction in the sulphuric acid concentration. This results in the maintenance of a pH close to neutrality within the bioprecipitation stage and thus, an optimal pH for SRB activity. Additionally, the substantially neutral pH will cause hydrogen sulphide to remain in solution, thus maintaining a redox potential sufficiently low for SRB viability, ie $< -300\text{mV}$.

The maintenance of a suitable redox potential by this method is common. Although the procedure has previously been used to maintain a suitable reactor pH (eg as in EP 436254A), it has not previously been used to buffer against influent acid flows having a pH as low as pH 1.0 as might be encountered from the acid leaching step described herein.

As a result of the production of hydrogen sulphide and metal sulphides during bioprecipitation, three different product streams may arise from the bioprecipitation process:

- (a) precipitated metal salts (eg sulphides and hydroxides) and some biomass;
- (b) aqueous hydrogen sulphide, soluble metal and sulphides together with some biomass;
- (c) gaseous hydrogen sulphide and carbon dioxide.

Gaseous hydrogen sulphide may be extracted by a venting means provided at or near to the top of the reactor. Aqueous hydrogen sulphide and other soluble sulphides may be separated from the sludge.

The metal sulphide sludge may be removed separately via a suitable drain in the reactor. The sludge may then be dewatered, collected and transported to another site, treated for metal recycle, or treated by a suitable

encapsulation process, eg biologically enhanced metal fixation.

The gaseous and aqueous hydrogen sulphide extracted is a valuable source of re-usable sulphur which may be utilised by the biochemical oxidation process described hereinafter.

During the initial stages of operation of the metal leaching step of the process according to the present invention, the leachate entering bioprecipitation will possess a neutral pH. Therefore, a portion of this liquor can be used to dissolve the gaseous hydrogen sulphide effluent produced from bioprecipitation.

The two aqueous hydrogen sulphide streams derived from bioprecipitation may be employed separately, or preferably combined, and oxidised within an enclosed bioreactor. The bioreactor may comprise a known system containing a consortium of naturally occurring sulphide oxidising organisms. Examples of micro-organisms known to oxidise soluble sulphides include: *Thiobacillus thioparus*, *T. neapolitanus*, *T. denitrificans* and *Thiomicrospira* species. Two routes are possible for sulphide oxidation:

- (a) direct oxidation to sulphuric acid and sulphates;
- (b) oxidation to elemental sulphur, which can if appropriate then introduced into the contaminated soil to produce sulphuric acid.

Oxidation to elemental sulphur requires an oxygen limited environment, but possesses the advantage of providing a sulphide free, pH neutral liquor that can be used to dissolve effluent hydrogen sulphide gas from bioprecipitation. The sulphuric acid liquor produced by direct oxidation is more versatile for use in subsequently contacting the contaminated soil.

As noted above, the process of the present invention includes one or more steps for the removal of organic contaminants from the said contaminated medium and this may be by a remediation process deployed in a similar

manner to that used for the metal removal process. In general, different micro-organisms are known to degrade different species of organic compound and appropriate microbial consortia may be selected according to the type(s) of compounds to be degraded but will generally be present within the contaminated material. The contaminated material is preferably analysed prior to treatment to ensure an appropriate consortium is already present or added to be present. Examples of degradative strategies which may be selected are given as follows.

As a result of the interest in and research performed in the prior art to investigate the microbiological degradation of organic contaminants, several known key strategies have emerged. The strategies employed are greatly influenced by oxygen which may either function as a preferred electron acceptor, or may enzymatically be incorporated into the molecule.

Alkanes - may be degraded aerobically by micro-organisms belonging to several genera including: *Pseudomonas*, *Nocardia*, *Mycobacteria*, and *Flavobacteria*. The degradation of such compounds initially involves the introduction of oxygen into the molecule by a monooxygenase enzyme. Subsequent conversion of the resulting fatty acids to aldehydes and the carboxylic acids enables further oxidation through the beta oxidation pathway (Gottschalk, 1986).

Alkenes and alkynes - can be degraded either aerobically or anaerobically. Aerobic degradation occurs by a mechanism similar to that for alkanes. However, the more reactive nature of the double and triple bonds also permits initial degradation of the molecule under anaerobic conditions by either hydration, or epoxidation reactions. Subsequent oxidation then proceeds via beta oxidation.

Halogenated aliphatic compounds - are susceptible to both aerobic and anaerobic degradation. Generally,

however, more highly halogenated compounds are more susceptible to anaerobic degradation.

Cyclic and aromatic compounds - are once again susceptible to both aerobic and anaerobic degradation. Under aerobic conditions the initial attack involves the insertion of a series of oxygen atoms into the molecule by oxygenase enzymes. Subsequent degradation occurs by either ortho or meta fission involving a further dioxygenase enzyme to achieve ring breakage. Halogenated compounds are degraded by a similar mechanism. The microorganisms involved in such degradations include: species of *Alcaligenes*, *Pseudomonas* and *Corynebacteria* which are able to degrade polychlorinated biphenyls (Unterman et al 1988) and *Flavobacteria* species which are able to degrade pentachlorophenol (Frick et al 1988).

Under anaerobic conditions substituted aromatic compounds are reduced to cyclohexanone. Ring cleavage is then achieved by hydration. Aromatic compounds with more than one chlorine atom are reductively dehalogenated prior to conversion to cyclohexanone.

Halogenated compounds - particularly those possessing more than one functional halogen group, are also subject to reductive dehalogenation. This involves the compounds acting as electron acceptors and results in chlorine atoms being eliminated from the molecule to be replaced by hydrogen's. Highly halogenated compounds eg hexachloroethane are strongly oxidised and possess greater electron affinities than molecular oxygen. As successive rounds of dehalogenation occur and electron affinities fall, the use of alternative electron acceptors such as oxygen and nitrate becomes probable, thus governing the conditions and groups of organisms that are able to effect degradation. Examples of organisms involved in reductive dechlorination include: *Pseudomonas*, *Alcaligenes* and *Clostridia* sp.

In contrast to metal removal, the mechanisms employed to degrade organic soil or land contaminants will be very site specific, as these will need to be tailored to the particular contaminants present within a site. However, some generalisations can be made:

1. The degradative process will be optimised to reduce and/or eliminate a range of organic compounds particularly VOC's (volatile organic compounds) and PAH's under aerobic or anaerobic conditions. These compounds will be mineralised to CO_2 and H_2O .

2. With the exception of a source of sulphate and possibly an anaerobic environment, the nutrients required to promote the growth of degradative organisms will be the same as during metal bioleaching and will be required at similar concentrations.

3. Near neutral pH conditions will be required to maximise the numbers and types of degradative organisms which can be grown.

4. Similar types of soil treatment equipment will be required for the degradation of organics, as are required during metals removal.

In some instances organic contaminants present together with metallic contaminants are desirably treated before significant acidification, or metal mobilisation within the contaminated material, as this could have a deleterious effect on the micro-organisms required in the organics degradation step.

Therefore, organics may initially be degraded during operation of the process according to the present invention prior to metal leaching. Further organics degradation may occur during metal leaching. Depending on the degradative requirement of the organic contaminants, the system may be operated aerobically, anaerobically, or a combination of the two. However, anaerobic operation would delay acidification of the contaminated material. Additionally, if large amounts of organic contaminants are

present it may be necessary to delay the acidification process until sufficient organic degradation has occurred. For instance for a halogenated compound such as trichloroethylene, anaerobic conditions may be maintained to allow reductive dechlorination to vinyl chloride which may subsequently be mineralised under anaerobic conditions. Following degradation of the majority of the organics, the metal removal system may then be started. Additionally, some of the organisms employed for metal removal may be capable of degrading particular contaminants eg phenolic compounds may be degraded by *Desulfobacteria* species.

The organics treatment step when applied to soil and the like may be carried out either in-situ or ex-situ as appropriate and as determined by the requirements of the metal leaching step. In ex-situ processes a nutrient solution is contacted with the soil following excavation, over an impermeable base, the leachate solution collected and recirculated following aeration if necessary.

In-situ processes for the treatment of soil or land contaminated with organics may involve either injecting, or spraying nutrients onto the contaminated area, thus avoiding excavation. Where aeration of the nutrient solution is necessary for contaminant degradation, air may be injected into the contaminated area, or an oxidising agent, eg hydrogen peroxide may be added to the nutrient solution. Leachate may be collected either in trenches, or using a system of recovery wells and recirculated.

The present invention therefore beneficially allows metal and organic contaminants to be removed from a contaminated medium using a single multistep biotreatment system. As the sulphur source may be at least partially recycled, thus allowing re-use of the process liquor, the process can conveniently be operated as a cyclical system. The present invention offers the following further advantages over prior art processes: (1) It provides a

permanent solution to the contamination problem. (2) It allows the simultaneous treatment of metal and organic contaminants. (3) In-situ and ex-situ treatment systems can be available and selected as appropriate. (4) The size of the secondary waste streams and therefore the cost of dealing with them is minimised. (5) It minimises the use of harsh chemicals which could harm the environment. (6) An opportunity to re-use certain metal contaminants is offered.

Embodiments of the present invention will now be described by way of example with reference to the accompanying drawings, in which:

Figure 1 is a diagrammatic cross-sectional view of a region of land being treated in-situ by a remediation process embodying the present invention together with equipment used in the process.

As shown in Figure 1, a region of land to be treated comprises a layer 1 of soil overlying an underground aquifer 3 below a level 2. The layer 1 incorporates a metal contaminated region 4 which has been produced by migration of contaminants from a waste sump 5 provided in the surface of the layer 1. The region 4 extends into the aquifer 3. A monitoring well 6 projects downward through the region 4 to enable measurements on the extent of contamination in the region 4 to be determined. The depth and dimensions of the contaminated region 4 have previously been determined using appropriate known analytical techniques, ground level is indicated by point 18.

Nutrients from a nutrient source 22 and, at a suitable stage in the process acid, which may be carried in a suitable carrier liquid, eg aerated water, are applied to the base of the empty sump 5. This application is carried out by a sprayer 7. This liquid is also applied via appropriately positioned injection wells 8 and through an infiltration gallery 9, so as to permeate through the

material in the contaminated region 4. The nutrients are initially selected to promote growth of appropriate micro-organisms to provide organics degradation under substantially neutral pH conditions using one or more of the methods described above. The nutrient addition is later modified to promote soil acidification. During this secondary treatment phase, elemental sulphur may also be added to and mixed into areas of shallow contamination such as the base of the sump 5 further to promote in-situ bioleaching of metal species.

In order to enable aerobic conditions to be developed and maintained within the contaminated region 4 air is blown by an air blower 21 attached to a series of vent wells 10, (one of which is shown) either to draw air through the contaminated region 4 in the layer 1 or to inject air into the ground water in the aquifer 3 or both. Additionally, the rate of nutrient addition may be varied to avoid or create anoxic conditions within the contaminated region 4 as appropriate. The plume or region in the layer 1 and aquifer 3 supplied with nutrients and ingredients in an aqueous medium is indicated by reference 20. This plume 20 encompasses the contaminated region 4 in the layer 1 and aquifer 3.

This treatment degrades organics and subsequently also produces acid metal leaching in the region 4 in the manner described above. This may continue over weeks or months until the soil in the contaminated region 4 is substantially free of contaminating organics and metals as determined from time-to-time by suitable analysis.

The products of both organics degradation and metal leaching are collected within a portion of a ground water flow in a direction X, either naturally occurring or artificially created, and are collected by and returned to the surface above the layer 1 via a series of recovery wells 11 (one shown) using appropriate pumps (not shown). The level 2 of the aquifer 3 may be adjusted by addition

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of water through an infiltration gallery 24 to assist water flow in the direction X.

The collected liquor is then delivered to a selected one of three locations, viz:

(a) a buffer tank 12 for aeration and addition of appropriate nutrients before re-application to the contaminated area. This is the principal route during initial operation of the process;

(b) a bioprecipitation reactor 13;

(c) a gas liquid contactor 14 to scrub hydrogen sulphide from the gaseous effluent from bioprecipitation.

Liquor enters the reactor 13 at its base and flows upward through the reactor 13. As it does so, sulphate reducing organisms present in the reactor 13 convert the influent sulphates to sulphides in the manner described above.

The gaseous effluent produced during bioprecipitation in the reactor 13 is passed through the gas-liquid contactor 14 connected to the reactor 13. The contactor 14 permits hydrogen sulphide recovery. The gas stream leaving the contactor 14 is passed through a secondary scrubber unit 19 and discharged to atmosphere.

Bioprecipitated sludge containing insoluble sulphides is collected in the base of the reactor 13 and transferred via a pipeline 15 to a separate treatment process, eg biologically enhanced metal fixation, or is dewatered and collected and delivered to another site for metal recovery. The liquor obtained by dewatering the sludge may either be returned for re-use in the metal bioleaching step of the process embodying the invention, or further treated and discharged.

The effluent liquor containing dissolved sulphides arising from bioprecipitation is extracted and combined with the aqueous sulphide stream arising from the gas/liquid contactor 14. The combined aqueous sulphide stream is then pumped through a gas/liquid contactor 16

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and into a sulphide oxidation reactor 17. The contactor 16 ensures that any gaseous hydrogen sulphide released by acid in the reactor 17 is re-dissolved by the alkaline influent liquor.

Within the oxidation reactor 17, the sulphide containing liquor is intimately mixed with suitable micro-organisms and oxidised to sulphate in the manner described above. The acid liquor produced is then transferred to the buffer tank or bioreactor 12 where further elemental sulphur may be added from a source 23 if required, and oxidised to sulphuric acid, by micro-organisms carried over from reactor 17 before re-addition to the contaminated material in the soil 1 in the manner described above (via the wells 8 and gallery 9 and sprayer 7). The added sulphurous material and nutrients forms a plume 20.

The metal removal treatment process is therefore cyclical and metal contaminants in the portion 3 of the soil layer 1 are, during various cycles of the metal removal process, gradually leached by the influent solution containing biochemically formed sulphuric acid and recovered as an insoluble sulphide formed in the bioprecipitation reactor 13.

A proportion of the sulphur is recovered by oxidation of sulphides in the oxidation reactor 17 and is re-used in the soil acid leaching of metal contaminants.

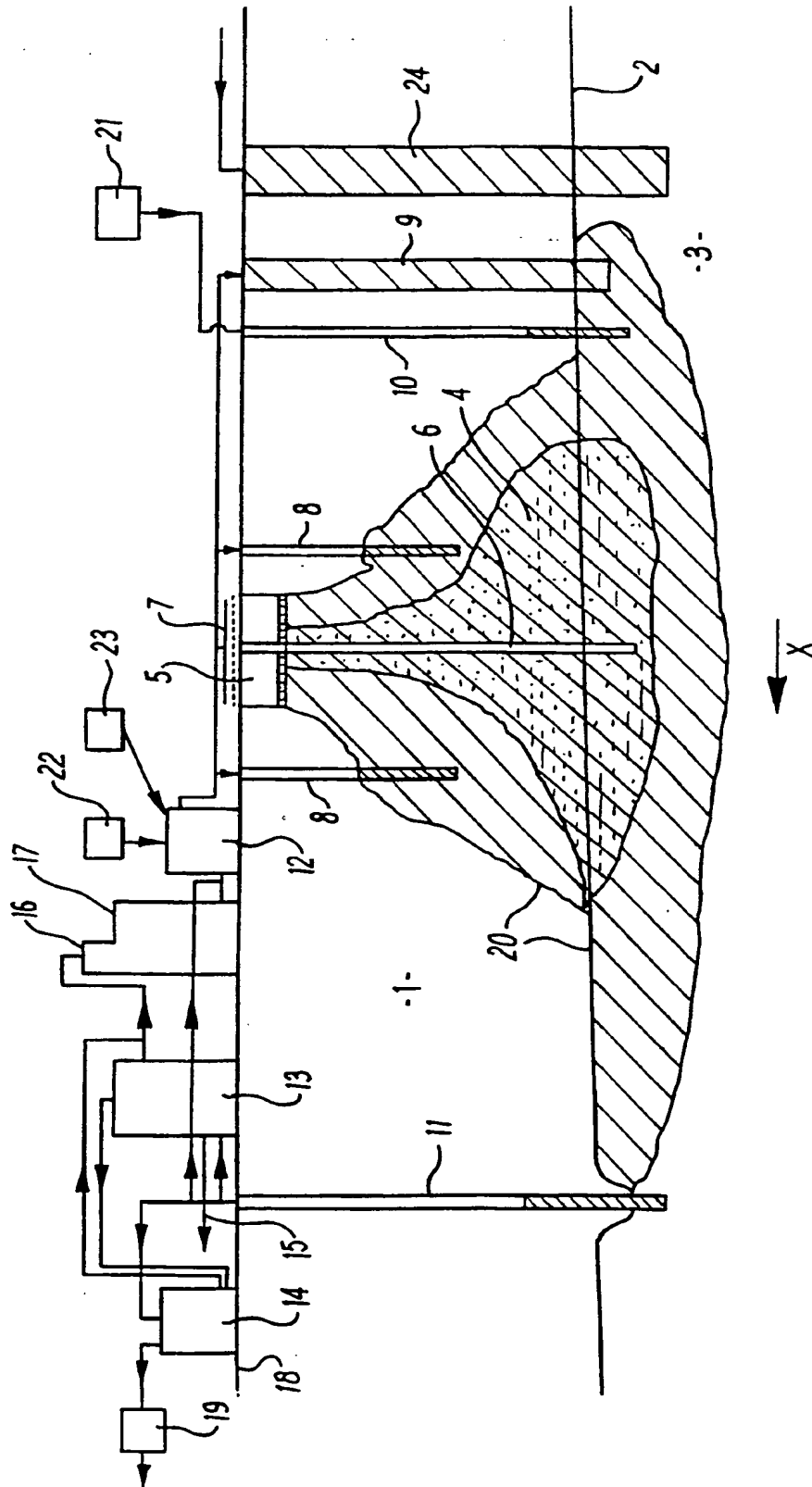
Claims

1. A process for the decontamination of a medium comprising a material contaminated with one or more organic species and one or more metal species comprises the steps of treating a body of the said medium by a process which breaks down the organic contaminant(s) by or through the action of microbial agents followed by treating the same body with microbially produced sulphuric acid so as to solubilise and leach the metal species as a metal sulphate and treating the leached metal sulphate by a bioprecipitation process which converts the said sulphate to one or more insoluble metal sulphides.
2. A process as in Claim 1 and wherein hydrogen sulphide produced during bioprecipitation is separated from the insoluble metal sulphides.
3. A process as in Claim 2 and wherein the hydrogen sulphide is oxidised to form a re-usable source of a sulphur-containing ingredient.
4. A process as in any one of the preceding claims and wherein in a first stage of the process wherein organic contaminants are biodegraded by microbial agents prior to the said acid treatment, the pH of the contaminated medium is maintained in the range 5 to 9.
5. A process as in Claim 4 and wherein the said organic contaminants are also broken down by the action of microbially produced sulphuric acid in the second stage of the process.
6. A process as in any one of the preceding claims and wherein the said medium comprises a particulate material selected from soil, rock particles, dredgings, sediments, sludges, process residues, slags and furnace dusts.
7. A process as in any one of the preceding claims and wherein the metal species comprises a radioactive or toxic heavy metal species.
8. A process as in Claim 6 or Claim 7 and wherein the said medium comprises soil which is treated in-situ.

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9. A process as in any of the preceding claims and wherein the metal species treatment part of the process is cyclical, the re-usable source of the sulphur-containing ingredient being microbially converted to sulphuric acid for re-use in the said medium.

10. A process as in Claim 9 and wherein the said microbial conversion to sulphuric acid is carried out in-situ in the medium being treated.



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INTERNATIONAL SEARCH REPORT

Intern. Application No.
PCT/GB 95/00287

A. CLASSIFICATION OF SUBJECT MATTER IPC 6 A62D3/00 B09C1/10 B09C1/02 C02F3/34 C22B3/00		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 6 B09C C02F A62D C22B		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DE,C,26 51 673 (BATELLE-INSTITUT) 21 February 1980 see claims ---	1,4,6
Y	DATABASE WPI Week 8916 Derwent Publications Ltd., London, GB; AN 89-119928 & JP,A,01 067 299 (NAKAYAMA) , 13 March 1989 see abstract ---	1,4,6
A	DE,A,41 17 515 (NOELL GMBH) 17 December 1992 see column 1, line 3 - line 14 see column 5; example 2 see claims 1,3-5 --- -/--	1,6
<div style="display: flex; justify-content: space-between;"> <input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex. </div>		
<div style="display: flex;"> <div style="flex: 1;"> <p>* Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="flex: 1;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>		
Date of the actual completion of the international search <div style="text-align: center; font-weight: bold;">9 May 1995</div>		Date of mailing of the international search report <div style="text-align: center; font-weight: bold;">24. 05. 95</div>
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+ 31-70) 340-3016		Authorized officer <div style="text-align: center; font-weight: bold;">Laval, J</div>

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DD,B,290 408 (WASSERVERSORGUNG UND ABWASSERBEHANDLUNG BERLIN) 29 May 1991 see the whole document ---	1,3
A	DD,B,249 155 (AKADEMIE DER WISSENSCHAFTEN DER DDR) 2 September 1987 see page 2, line 20 - line 52 see claims 1,2 ---	1
A	US,A,5 263 795 (J. COREY) 23 November 1993 see column 2, line 14 - column 4, line 64 see figures 1,2 ---	1,6,8
A	US,A,4 108 722 (D. STOVER) 22 August 1978 see claims ---	1,6,8
A	US,A,4 789 478 (N. REVIS) 6 December 1988 see column 2, line 34 - column 3, line 2 see examples 4,5 see claims 1,12 ---	1,6,7
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A	EP,A,0 436 254 (SHELL) 10 July 1991 cited in the application -----	

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